

FATE OF NERVE AGENT SIMULANTS ON CONCRETE

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ABSTRACT

The nerve agent VX (O-ethyl S-[2-(diisopropylamino)ethyl]methylphosphonothiolate) has been shown to decompose in contact with concrete surfaces. We have previously shown that ^{31}P NMR can be employed to study 1) the adsorption of VX into concrete; 2) the decomposition kinetics; and 3) detect decomposition products. Recently reported results show a dramatic effect of the VX decomposition kinetics on droplet size, with 0.01 μL droplets reacting within a few hours in contrast to months observed for VX drop sizes on the order of several μL . The objective of this paper is to probe the effects of temperature, moisture, concrete source and droplet size on the rate of hydrolysis. In the present study, ^{31}P NMR showed that the hydrolysis of nerve agent simulant DMMP (dimethyl methylphosphonate) on concrete increased with increasing temperature, amount of water added, and pH of the concrete used. No effect on hydrolysis rate as a function of droplet size in the 0.05 to 2.0 μL range was detected.

INTRODUCTION

The rate of decomposition of chemical warfare agents on substrates commonly present in a battlefield or urban environment, such as concrete and sand, is important since the decomposition to non-toxic products will determine when the area will be safe to reenter without protective gear. The nerve agent VX (O-ethyl S-[2-(diisopropylamino)ethyl]methylphosphonothiolate) has been shown to decompose in contact with concrete surfaces.¹ This decomposition was shown to proceed with an initial hydrolysis of 12% of the VX that had a half-life of 2.2 hours, followed by a subsequent decomposition that had a half-life of 28 days to 3 months on crushed and monolithic concrete, respectively.² Recently reported results show a dramatic effect of the VX decomposition kinetics on droplet size, with 0.01 μL droplets reacting within a few hours³ in contrast to months observed for VX drop sizes on the order of several μL . Differences between these experiments were the source and pH of the concrete, drop size, neat versus dissolved VX, and crushed versus chunk concrete. This work involves a systematic study of the variables of time, temperature, pH, moisture, concrete source, and drop size on the hydrolysis of the simulant DMMP. The data obtained from these studies will be used as a guide for future experiments with VX.

EXPERIMENTAL

MATERIALS. Dimethyl methylphosphonate, (DMMP), CAS# Registry Number 756-79-6 was purchased from Aldrich Chemical Company and used as received. ^{31}P NMR of the starting materials indicated that it was the correct compound. Concrete samples 8GWW, CB1-27C, and CB1-37C were all made using sieved Quikrete® concrete that had been sieved through a 10-mesh screen to remove all of the large aggregate. The concrete:water ratio (by weight) was 4.3:1 for concrete CB1-27C and 4.5:1 for concrete CB1-37C. One method of characterizing the samples was

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to put the concrete in water for 1-3 hours and measure the pH; 8GWW and CB1-37C gave a pH of 8-9, whereas CB1-27C gave a pH of 9.5 to 11. Concrete CZ was received from the Czech Republic (the aggregate in these samples was less than 2mm diameter, and its pH was ~11).

METHODS. The concrete chunks were inoculated with DMMP and then with water, which was put directly on top of the DMMP. In general, a total of 4 μL DMMP were used, with 8, 24, or 40 μL water, which gave molar ratios of 12, 36 or 60 respectively. Thus, all of the kinetic measurements were pseudo-first-order in $[\text{H}_2\text{O}]$. The sample was put into a 10mm NMR tube, and the initial $^{31}\text{P}\{^1\text{H}\}$ NMR total integrated peak area was measured using a 10mm liquids probe on a Varian Inova wide bore instrument. After allowing an estimated half-life of time to pass, the $^{31}\text{P}\{^1\text{H}\}$ NMR total integrated peak area was remeasured; it was not possible to obtain resolution between reactant and product, since the peaks were about 7,000 Hz wide. The overall signal intensities indicated that at least 80% of the original ^{31}P nuclei were detected. The sample was then covered with ca. 1 mL water, and allowed to sit for 30 to 180 minutes to allow the compounds to diffuse from the concrete. The solution peaks were 20 to 50 Hz wide, and thus the individual components could be identified, using $^{31}\text{P}\{^1\text{H}\}$, ^1H and ^{31}P NMR. $^{31}\text{P}\{^1\text{H}\}$ NMR total integrated peak area was measured for all components and compared to the original; all of the ^{31}P present initially was found in the aqueous solution. Rate constants were derived from the %DMMP remaining (the reaction in solution was shown to be first-order in [DMMP]; it was assumed that the reaction on the concrete is also first order. Only reactions that had 10% to 90% DMMP present were used for these calculations. Chemical shifts were measured relative to an external phosphoric acid standard.

Statistics. JMP Statistical Discovery Software, Professional Edition, by SAS Institute Inc. was used for the experimental design and data analysis.

RESULTS AND DISCUSSION

STABILITY OF DMMP ON AN AMBIENT CONCRETE CHUNK

The ^{31}P NMR spectrum of the DMMP on ambient concrete was measured as a function of time; the parameters observed were the ^{31}P relaxation time, T_1 , total integrated peak area, line width and chemical shift.

The T_1 was largely a function of the concrete used, and no trend with time was seen (Figure 1a). The T_1 was less than 0.1 seconds for concrete G8WW, 0.5 to 2 seconds for concrete CB1-27C, and 0.1 to 0.5 second for concrete CB1-37C. Possible reasons for the short T_1 in concrete versus the 12s T_1 in solution are paramagnetic impurities and/or restricted mobilities in the concrete. T_1 was also measured as a function of drop size (Figure 1b). Statistical analysis of the groupings of drop size using the Student t-test at $\alpha=0.05$ showed that the 0.1 and 0.25 μL samples were significantly different from the 0.5 and 2 μL samples.

The total integrated peak area of the DMMP shifted slightly based on the exact amount of DMMP that was added to the sample. Thus, the average of all of the integrated peak areas for that sample was taken, and each individual integrated peak area was normalized by the average, to give a normalized intensity. If there were no effect of sample age on the total integrated peak area, the normalized integrated peak areas would be randomly distributed around the 1.0 horizontal line (Figure 2a). The expected range would be ~20%, which represents the repeatability of this experiment. The three samples that were examined in detail all have intensities within the anticipated 20% range, but the intensity gradually diminishes with time. Possible explanations are a slow evaporation of the DMMP or a product that has an extremely broad line width and/or a very long T_1 .

The line widths of DMMP on a number of concrete samples run in the liquid probe were measured. The range was 4,000 to 10,000 Hz; most peaks were 6,500 to 8,500 Hz wide (Figure

2b). This broadness precluded the resolution of DMMP and its hydrolysis product, MMP (Figure 3). The chemical shifts observed ranged from 34 to 46 ppm, regardless of the concrete used (Figure 4). By comparison, the chemical shift of DMMP in distilled water and a variety of aqueous buffers ranged from 38 to 41 ppm.

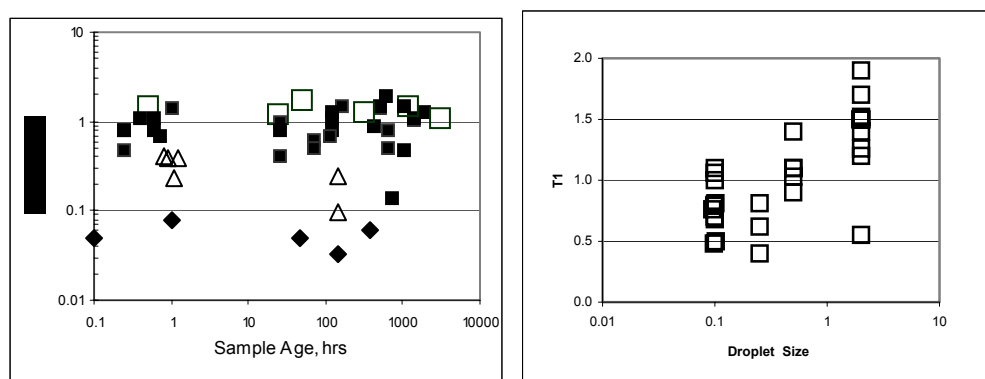


Figure 1. a) Plot of relaxation time, T_1 , versus the sample age. Code: \square =93G, \blacksquare =CB1-27C, \blacklozenge =8GWW, \triangle =CB1-37C. b) Plot of T_1 versus Droplet Size for 4 μ L DMMP on concrete CB1-27C.

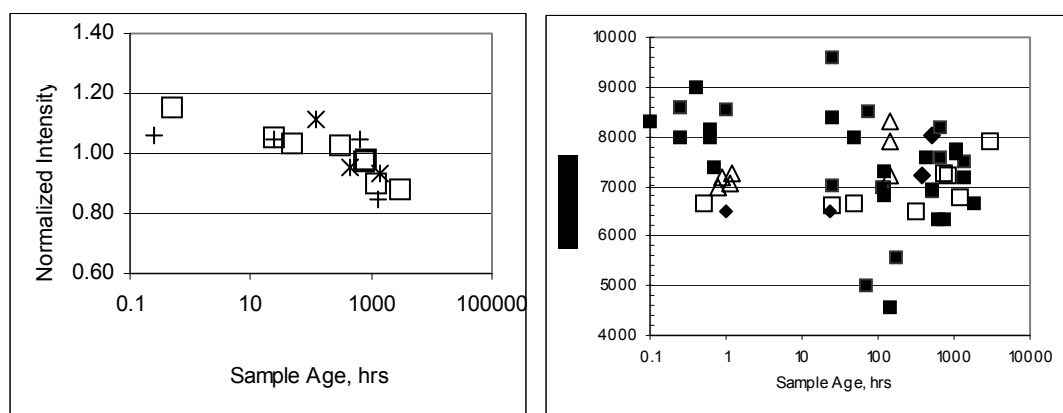


Figure 2. a) Normalized Intensity versus time for select samples of DMMP on concrete CB1-27C: \square =93G, +=131A, *=77B. b) Plot of the peak line width versus sample age. Code: \square =93G, \blacksquare =CB1-27C, \blacklozenge =8GWW, \triangle =CB1-37C.

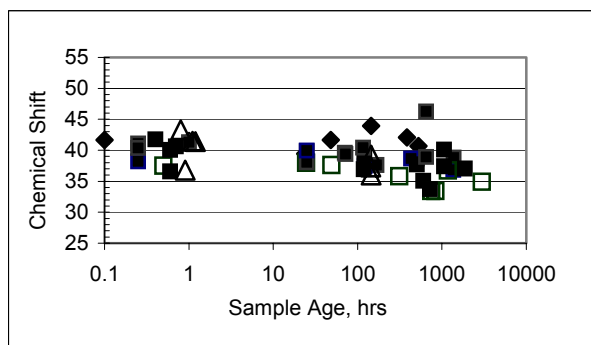


Figure 3. Chemical shift of DMMP on Various concrete samples versus sample age. Code: \square =93G, \blacksquare =CB1-27C, \blacklozenge =8GWW, \triangle =CB1-37C.

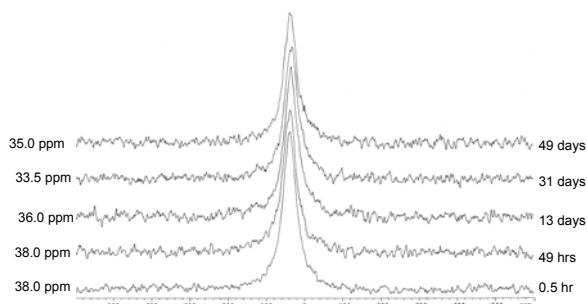


Figure 4. Chemical shift evolution of DMMP on concrete chunk CB1-27C with added water.

KINETICS OF DMMP HYDROLYSIS ON A MOIST CONCRETE CHUNK

The rate of DMMP hydrolysis as a function of added water and temperature was measured by incubating the DMMP and water on the concrete, then removing the reactant and product from the concrete with water. The extent of the reaction was calculated from the relative %DMMP remaining, as measured by ^{31}P NMR. The water and temperature parameters were varied according to an experimental design. The data were fit to the equation:

$$\text{Log } t_{1/2} = a + b \cdot \mu\text{L water} + c \cdot \text{temperature}.$$

The model was accepted if it had $R^2 > 0.9$; significant factors were chosen as those with $P < 0.05$.

An acceptable model (Figure 5) was found for concrete CB1-37C ($R^2 = 0.92$):

$$\text{Log}_{10} t_{1/2} = 4.0 - (0.014 \cdot \mu\text{L water}) - (0.038 \cdot \text{temperature}).$$

The standard errors of the coefficients were 0.2, 0.003 and 0.004 respectively.

The data were analyzed using the \log_{10} of the half-life because the range of the data is large and because the time periods of interest are minutes, hours and days rather than one hour versus ten hours. Thus, the data are sufficient for order of magnitude predictions, but cannot precisely predict if a reaction will take 20 or 40 hours. When the calculated and observed $\log_{10}(t_{1/2})$ were compared, the ratio ranged from 0.5 to 2.0, with a mean of 1.0. Some of the variability in the replicate measurements, (which was also reflected in the standard errors of the coefficients in the equation) was due to the fact that concrete is a heterogeneous material. Although much of the aggregate was removed from concrete CB1-37C before use, since the samples were small, heterogeneity was a likely factor in the variability of the half-lives.

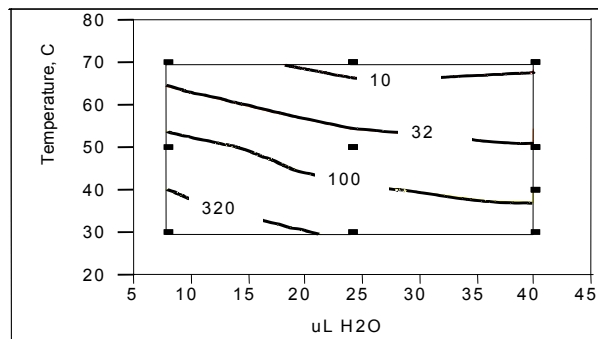


Figure 5. Plot of temperature vs. μL water, the contours are the half-lives, in hours, for DMMP hydrolysis on concrete CB1-37C. The rectangles show the conditions under which the data was collected.

EFFECT OF DMMP DROPLET SIZE ON HYDROLYSIS RATE

These experiments were performed at a constant temperature and droplet sizes of 0.05, 0.2 and 2.0 μL with 40 μL water on concrete CB1-37C; the hydrolysis rate was not affected by the drop size (Figure 6a).

ACTIVATION ENERGY FOR DMMP HYDROLYSIS ON CONCRETE CHUNKS

The activation energy was calculated using the Arrhenius equation. These two equations are generally applied to homogeneous reactions in solution. To the extent that the reactants are liquids within the pores of the concrete, these equations may be applied here. The equations used were:⁴
 $k = A \exp(-E_a/RT)$ and $\ln k = \ln A - E_a/RT$
 where k = rate constant, A = preexponential factor, R = gas constant, E_a = activation energy, and T = temperature in Kelvin.

The activation energy, E_a , was derived from the slope divided by the gas constant R from a plot of $\ln k$ vs $1/T$, and the preexponential factor A was calculated from the intercept of the line (Figure 6b, Table 3).

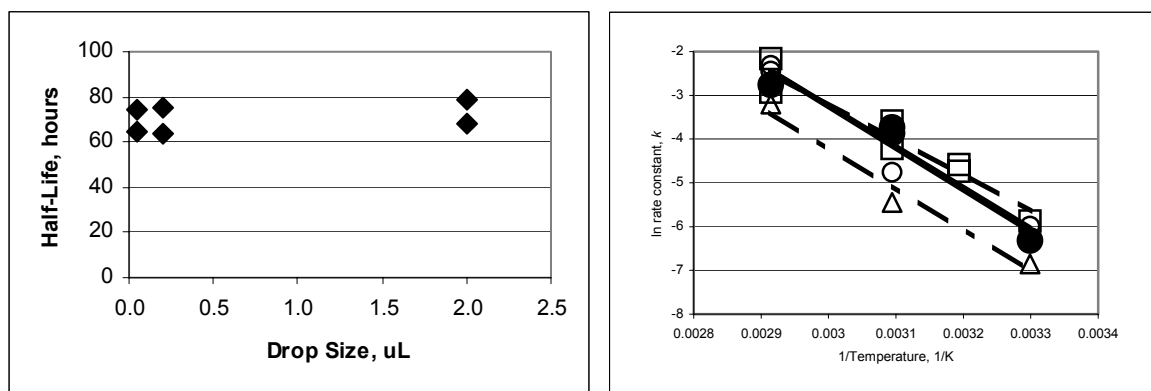


Figure 6. a) Half-life for DMMP hydrolysis at 40°C as a function of droplet size. b) Arrhenius plot of $\ln k$ vs $1/T$. \blacklozenge = CB1-27C, 24 μL water, \triangle = CB1-37C, 8 μL water, \circ = CB1-37C, 24 μL water, \square = CB1-37C, 40 μL water.

Table 1. Summary of Activation Energy Parameters

Concrete	μL water	E_a kJ mol^{-1}	A , $\text{M}^{-1}\text{hr}^{-1}$	-slope, K
CB1-37C	8	78.5	$3.1\text{E}10$	9446
CB1-37C	24	79.1	$9.7\text{E}10$	9519
CB1-37C	40	68.4	$2.2\text{E}9$	8230
CB1-27C	24	77.6	$5.8\text{E}10$	9341

DMMP HYDROLYSIS IN AQUEOUS SOLUTION

The purpose of these experiments was to simulate the hydrolysis in the presence of heavy rainfall. The rate generally followed that of DMMP in pH-buffered solution, and was base-catalyzed.

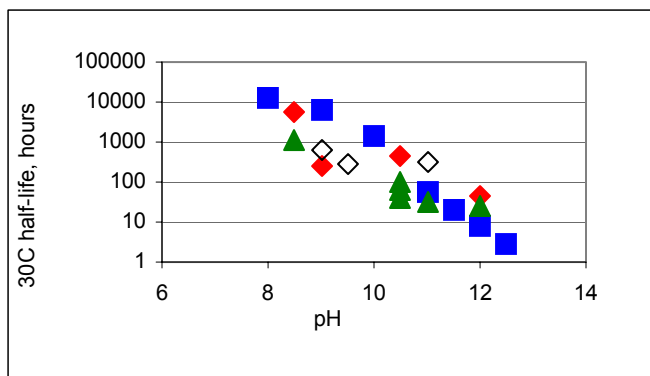
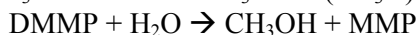
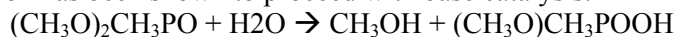


Figure 7. Plot of 30°C half-life versus pH. ◆ = Concrete, 40 μL water; ◇ = Concrete, 8 μL water, ■ = Aqueous solution; ▲ = Concrete in 1 mL water.

PRODUCT ANALYSIS

The reaction of interest was the hydrolysis of DMMP, which has been well documented in the literature. Methyl methylphosphonic acid, MMP, is the product; the second hydrolysis does not occur. The reaction has been shown to proceed with base catalysis.^{5,6}



In this work the products were identified using ^{31}P , ^1H -coupled and ^1H , ^{31}P -coupled NMR spectroscopy (Figure 8).

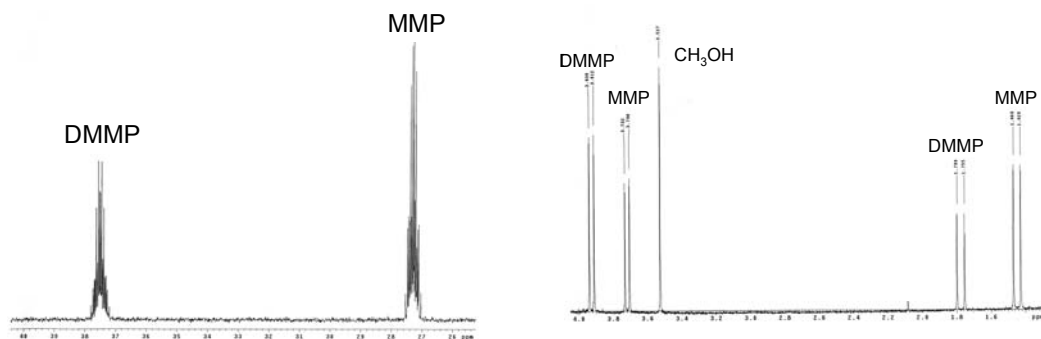


Figure 8. a) ^{31}P , ^1H -coupled NMR spectrum and b) ^1H , ^{31}P -coupled NMR spectrum of DMMP and MMP in aqueous basic solution.

CONCLUSIONS

Samples of concrete from different sources gave different rates for the hydrolysis of DMMP. One difference found between the concrete from various sources was that the pH imparted to water in which they were placed differed; it ranged from 8 to 11 pH units.

The hydrolysis of DMMP in aqueous solution increased with increasing pH; its hydrolysis on concrete chunks followed this trend.

For concrete CB1-37, it was possible to quantify the hydrolysis rate in terms of the temperature and amount of water added.

The activation energy of the hydrolysis of DMMP did not change with the concrete used, but decreased when more water was present.

Changing the droplet size from 0.05 μL to 2.0 μL had no affect on the DMMP hydrolysis rate.

This work will be extended to include surface area and pore size characterization of the concrete samples, and more types of concrete and aggregate will be added. Smaller droplets will be used, and studies of VX and the simulant O,S-diethyl phenylphosphonothioate (DEPPT) will be performed.

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